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Biodiesel resources and production technologies – A review

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ABSTRACT

The environmental concern and availability of fuels are greatly affecting the trends of fuels for transportation vehicles. Biodiesel is one of the options as alternative transport fuel. This can be produced from straight vegetable oils (SVOs), oils extracted from various plant species and animal fats. Amongst many resources, availability and cost economy are the major factors affecting the large scale production of the biodiesels. The transesterification is one of the production processes for biodiesel, but incomplete esterification of all fatty acids in the starting material, lengthy purification methods such as water washing, relatively long reaction times, contamination and separation difficulties associated with co-production of glycerol and saponification of the starting material under certain reaction conditions are still being major challenges in the biodiesel production. Technological advancement and enhanced production methods are the demand of present time for large scale and sustainable production of biodiesel. In the present paper, comprehensive review on its production process, feed stock and its applications have been made. From many case studies it was concluded that engine performance with B20 biodiesel blends, and mineral diesel were found comparable.

Contents

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1. Introduction

Rising petroleum prices, increasing threat to the environment from exhaust emissions and global warming have generated intense international interest in developing alternative non-petroleum fuels for engines. Biofuel is one of the options to fulfil the need as transport fuel. It received attention as environmental friendly renewable substitutes fuel [1,2]. Biofuel, sometimes refer as green energy sources. Green energy, loosely defined as the form and utilisation of energy that has no or minimal negative environmental, economic and societal impact, is essential to achieve the ultimate goal of sustainability. It provides an important option for meeting clean energy demand for both industrial and non-industrial applications. Green energy is consequently, a major factor in future sustainable development and world stability [3]. Biodiesel has the potential to reduce emissions from the transport industry, which is the largest producer of greenhouse gases. The use of biodiesel also reduces the particulate matter released into the atmosphere as a result of burning fuels, providing potential benefits to human health [4].

2. What is biodiesel?

Biodiesel, a mono alkyl ester (methyl or ethyl ester) of long chain fatty acids derived from renewable lipid such as vegetable oils and animal fats, can be used as a substitution fuel for traditional diesel in any compression ignition (diesel) engines with little or no modification [5–7]. Biodiesel is a chemically modified alternative fuel for use in diesel engines, derived from vegetable oils and animal fats. Blending/dilution, microemulsification, thermal cracking and transesterification are the commonly adoptable methods to convert those vegetable oils as fuel in CI engine. Biodiesel is produced commercially by the transesterification of vegetable oils with alcohol. Methanol or ethanol is the commonly used alcohols, which can be produced from biomass sources, for this process. The direct use of alcohols as fuel causes corrosion of various parts in the engine. The transesterification process solves this problem [8].

The term biodiesel was originally coined to describe unmodified vegetable oils that could substitute for diesel fuel (DF). Industrial use of biofuels started in the 1880s. Rudolf Diesel designed a prototype of the diesel engine, received a German patent (28 Feb. 1892), and demonstrated a workable engine in 1897. The first public demonstration by the French Otto Company of a small diesel engine operated on straight peanut (*Arachis hypogaea*) oil was seen at the World Fair in Paris of 1900 [9]. The diesel engine's inventor, Rudolf Diesel, viewed that the future of his engine (in contrast to those operating on steam) would be connected to fuel use derived from biomass, in particular plant oils (such as peanut and castor oil) and animal fats. Initially, straight vegetable oils, with high viscosity were used in bigger engines. But in the 1920s, technological changes made possible much smaller diesel, which required lower viscosity fuels, injected by small injectors.

At the same time, the introduction of relatively cheap medium-weight diesel fuels from fossil origin produced by the upcoming petroleum industry temporarily put a halt to the commercial viability of biofuels. Since 1930s the diesel engine has been fine-tuned to run on the diesel fraction of crude oil, which consists mainly of saturated hydrocarbons. As a result, modern diesel engines do not run satisfactorily on a straight vegetable oils (SVOs) feedstock because of problems of high viscosity, deposit formation in the injection system and poor cold-start [10]. Four techniques can be used to reduce the viscosity of vegetable oils; namely heating/pyrolysis, dilution/blending, micro-emulsion, and transesterification [11,12]. Now, the fuel trend is shifting towards the renewable sources, like biofuels. Many countries have started utilisation of biodiesel as fuel for transportation and energy generation. Table 1 shows the long-term goal set by various countries worldwide [10].

3. Feed stocks for biodiesel production

Potential renewable raw materials for biodiesel production are edible and non-edible SVOs, animal fats and oils, recycled or waste oils, by-products of the edible oil and dairy industries and other saturated and unsaturated fatty acids varying in carbon chain length and degree of unsaturation. Selection criteria of vegetable oils are: availability, cost, oil quality (composition) and product shelf-life.

There are more than 350 oil-bearing plants identified (with thousands of sub-species) that could be used to grow a new crop of fuel every year. The productivity of perennials is higher; they avoid erosion and can also be cultivated in mountain areas. Some species can be harvested more than once a year. The fuel potentialities of many vegetable oils (including castor, grapeseed, maize, camelina, pumpkinseed, beechnut, rapeseed, lupin, pea, poppyseed, peanut, hemp, linseed, chestnut, sunflower seed, palm, olive, soybean, cottonseed, shea butter) were considered as early as 1939 [10,13]. A shift from annual energy crops, which need to be replanted and harvested every year, to perennial crops (e.g. palm, *Jatropha*) is observed. Raw materials for modern biodiesel production were outlined recently [14]. Table 2: shows a selection of suitable biodiesel feedstocks on priorities basis, at present mainly RSO, SNO, SBO and PMO. New sources are HOSNO, rapeseed varieties.

3.1. Fractionation

Fractionation is used in the oils and fats industry to physically separate oils into high-melting 'stearin' fractions and lower-melting 'olein' fractions. Palm oil is most widely fractionated (see Fig. 1). The main triglycerides in palm oil can be grouped into: trisaturated triglycerides – typically PPP (palmitate–palmitate–palmitate); monounsaturated triglycerides – typically POP (palmitate–oleate–palmitate); and polyunsaturated triglycerides – typically POO (palmitate–oleate–oleate). These three groups also correspond roughly to the three main fractions produced from palm oil-stearin (PS), mid-fraction, and olein (POo).

Table 1
Long-term (national) goals in energy policy.

Challenger	Target(s)
World	Reduction in GHG emissions by 5.2% on 1990 levels throughout the 2008–12 period
Germany	Biodiesel target of 10% by 2015
	Reduction of GHG emissions by 40% by 2020 against 1990 levels
P.R. China	Share of 10% renewable energy by 2010, 15% by 2020
UK	Renewable transport fuels accounting for 5% in 2010 and 10% in 2015
	Reduction in CO_2 emissions by 26–32% (2020) to 80% (by 2050) against 1990 baseline
USA	Soya biodiesel share of 4% in 2016
	Replacement of 15% of current gasoline consumption by 2017[a]
India	Share of 10% renewable energy by 2012

[a] State of the Union 2007.

Table 2
Selection of suitable biodiesel feedstocks.

Top ten oilseeds	Other oil crops	New varieties	Animal fats and used oils
Soybean	Camelina	HO[a] sunflower	Tallow
Cottonseed	Hemp	HO[a] rapeseed	Lard
Groundnut	Olive	LL[b] rapeseed	Poultry fats
Sunflower	Jatropha	HEA[c] rapeseed	Rendered fats
Rapeseed	Corn		Used frying oil
Sesame			
Oil palm			
Coconut			
Linseed			
Castor			

[a] High oleic.
[b] Low linolenic.
[c] High erucic acid.

A common fractionation process is the separation of palm mid-fraction from palm olein. Palm olein (POo) is the liquid fraction derived from the fractionation of palm oil, and palm stearin (PS) the high-melting (hard) fraction. Palm stearin and palm kernel olein are both products of the palm oil industry that presently have limited use.

Free fatty acids are released naturally in crude palm oil (CPO) and can be increased by the action of enzymes in the palm fruit and by microbial lipases. During storage, FFAs are produced by the reaction of oil with water. Standard specifications for the FFA content (as palmitic acid) are 5% maximum in CPO and 0.1% maximum in refined–bleached–deodorised (RBD) oils, respectively. Routine procedures to determine the FFA content in vegetable oils are AOCS Official Methods Aa 6–38 and Ca 5a-40, as well as FTIR analysis [15].

3.2. Minor edible oil crops

Various alternative edible oils have suitable fatty acid compositions for use in biodiesel applications but are not expected to find large-scale application due to their high price and/or limited availability.

- **Argan oil** from the oil fruit of *Argania spinosa* L. (Sapotaceae), an endemic tree located mainly in South-West Morocco, is well known for its cosmetic, pharmaceutical and nutritional virtues.
- **Tigernut** or yellow nut-sedge (*Cyperus esculentus* L.) is a fast growing root crop, commonly found wild and cultivated in Northern Nigeria, which yields oil (also called chufa oil) with high oleic acid content (68.8%) and low acidity (0.4 mg KOH/g).
- **Cottonseed oil** (CSO) is a vegetable oil extracted from the seeds of the cotton plant (*Gossypium herbaceum*) after the cotton lint has been removed.
- **Dark-coloured crude rice bran oil** (CRBO) is difficult to refine because of its high content of free fatty acids (up to 60%), unsaponifiable matter and colour. RBO is not considered as an edible oil all over South-East Asia.
- **Corn oil** was considered as a fuel for biodiesel engines already in 1952 [16], historically it has not been a viable biodiesel feedstock due to its relatively high cost and high value as edible oil.
- ***Sesamum indicum* L** (sesame) is a herbaceous oilseed crop of the Pedaliaceae family.
- **The tea plant oil**, the tea plant (*Camellia sinensis*), cultivated mainly for its leaves, is a perennial, evergreen shrub and produces large seeds which contain approximately 30% oil.
- Industrial-grade crude corn oil is not available on the spot market, it is offered at a price discount because of its composition. Compared with other vegetable and rendered oils, it is high in FFA content (12–17 wt%), as well as in waxes and other chemicals that make it unsuitable for human consumption.

4. Biodiesel production

Biofuels can be produced from a variety of bio-feedstocks, they are renewable, sustainable, biodegradable, carbon neutral for the whole life cycle and environmentally friendly; they encourage

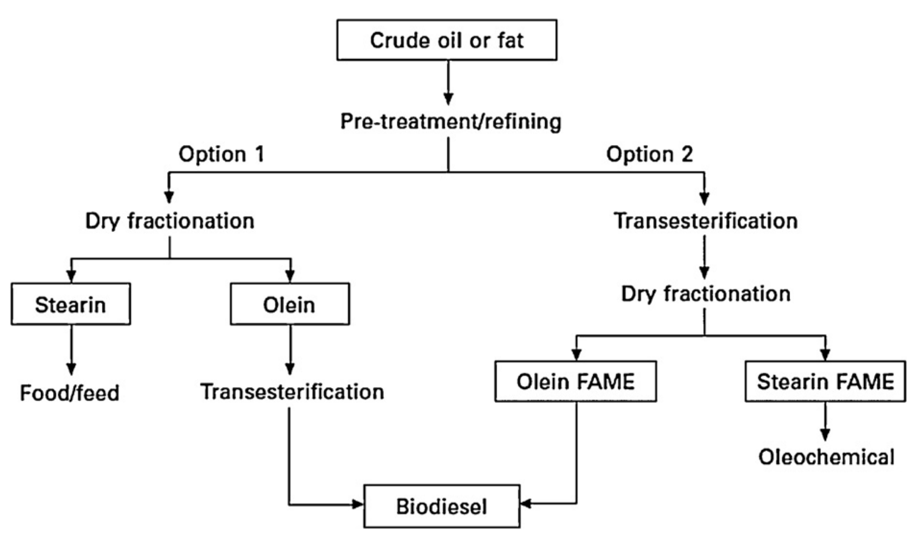


Fig. 1. Fractionation of palm oil or crude animal fat [10].

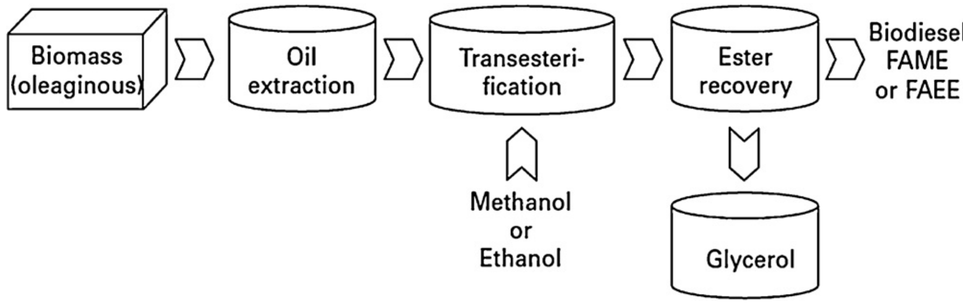


Fig. 2. First-generation biodiesels formation.

green industries and agriculture and are applicable as motor fuels, without or with slight engine modifications. Several biofuels, including bioethanol, biomethanol, biodiesel and biohydrogen, appear to be attractive options for the future of the transport sector. The production of biofuels is expected to rise steadily in the next few decades [17]. Biodiesel, namely fatty acid methyl esters (FAME) is an alternative diesel fuel [18,19]. At present, about 35% of the world's primary energy demand is met by petroleum, and the world petroleum demand in 2009 was 84 million barrels/day. According to the estimates of the International Energy Agency, demand will reach 90 million barrels/day by 2014, an increase of 7% on 2009 levels or 5 million barrels/day, with most of the increase in demand centred in China and Asia. With a reserves-to-production ratio of about 53 years, there is a concern of depletion. There is an urgent need to encourage the use of currently available biofuels as an intermediate step to prepare the world economy for more efficient alternatives in the transport sector [20].

Biodiesel (chemical name: fatty acid methyl/ethyl esters) is obtained by chemically modifying the straight vegetable oils (SVO), a process known as transesterification. Transesterification is a chemical reaction in which methanol or ethanol is reacted with SVO in the presence of a catalyst to produce fatty acid esters and glycerol. This process changes the properties of the vegetable oil in to a diesel like fuel [21]. Industrially, biodiesel (consisting of mixtures of medium- to long-chain fatty acid alkyl esters, mainly methyl esters: FAMEs) is produced by relatively complex (catalytic) alcoholysis (transesterification) of vegetable oils and animal fats. Fig. 2 shows the first-generation biofuels formation steps [10].

4.1. Low-viscosity formulations

Oils/fats contain high saturated fatty acids and cannot be used as fuel in a diesel engine in their original form. Viscosity is an important factor in predicting the performance of potential alternative diesel fuel sources. Standard fuel specification ASTM D 975 for petrodiesel may be used to evaluate the suitability of fuel compositions for compression-ignition engines. The kinematic viscosity limits (at 313 K) of petrodiesel fuel, namely 1.9–4.1 mm^2/s for DF2 (ASTM D 975) and 2.0–4.5 mm^2/s for the European petrodiesel standard (EN 590), are lower than those of biodiesel.

Direct use of vegetable oils and/or oil blends is generally considered to be unsatisfactory and impractical for both direct injection and indirect type diesel engines because of their relatively high kinematic viscosities and low volatilities. Various methods have been considered to gain sufficient engine compatibility for vegetable oil and animal fat-derived high-quality diesel fuels, including derivatisation (transesterification, hydrotreating, ozonation), pyrolysis/gasification, dilution, blending and microemulsification.

The process of transesterification removes glycerol from the triglycerides and replaces it with an alcohol. The process decreases the viscosity but maintains the cetane number and heating value. By transesterification the viscosity of vegetable oils is reduced from about 10 to 15 times that of No. 2 diesel fuel to about twice that of No. 2 diesel for methyl esters, which is low enough to be used as diesel fuel. Other physical properties of FAME, such as cloud point and pour point, are considerably higher than No. 2 diesel fuel, which limits their use as an alternative to diesel fuel. However, up to 30 vol% of methyl esters in diesel fuel does not significantly change the cold-flow properties of the fuel [22].

4.2. Transesterification processes for biodiesel production from oils and fats

Ester formation constitutes one of the most important classes of reactions in value-added processing of animal fats and vegetable oils. Typical schemes for ester formation include:

$$\mathrm{ROH} + \mathrm{R'COOH} \rightarrow \mathrm{R'COOR} + \mathrm{H_2O} \quad \text{(esterification)}$$

$$\mathrm{ROH} + \mathrm{R'COOH''} \rightarrow \mathrm{R'COOR} + \mathrm{R''OH} \quad \text{(alcoholysis)}$$

$$\mathrm{RCOOR'} + \mathrm{R''COOR''} \rightarrow \mathrm{R'COOR'''} + \mathrm{R''COOR'} \quad \text{(transesterification)}$$

$$\mathrm{RCOOR'} + \mathrm{R''COOH} \rightarrow \mathrm{RCOOH} + \mathrm{R''COOR'} \quad \text{(acidolysis)}$$

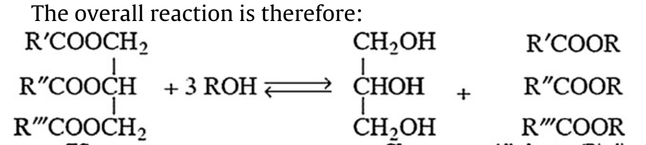
Transesterification of vegetable oils and animal fats is an equilibrium reaction consisting of a number of consecutive, reversible reactions in which a triglyceride is converted stepwise to diglyceride (DG), monoglyceride (MG) and finally glycerol (GL), as follows:

$$\text{Triglyceride(TG)} + \mathrm{ROH} \leftrightarrow \text{Diglyceride(DG)} + \mathrm{R'COOR}$$

$$\text{Diglyceride(DG)} + \mathrm{ROH} \leftrightarrow \text{Monoglyceride(MG)} + \mathrm{R''COOR}$$

$$\text{Monoglyceride(MG)} + \mathrm{ROH} \leftrightarrow \text{Glycerol(GL)} + \mathrm{R''COOR}$$

The overall reaction is therefore:



Generally speaking, there are two methods of transesterification reaction, namely with or without a catalyst. After (catalytic) transesterification of triglycerides, the products are a mixture of esters, alcohol (catalyst), tri-, di- and monoglycerides, glycerol (by-product) and salts. Transesterification does not alter the fatty acid composition of the feedstocks. Consequently, biodiesel reflects the composition of the vegetable oil under study, specifically the fatty acid profile. Intensification between oils can provide a means of varying the fatty acid structure of the base vegetable oil. For example, a broader spectrum of possible biodiesels has been produced by interesterification/transesterification between coconut/canola

and peanut/canola oil mixes [10]. Transesterification can be carried out as a batch process, as a continuous or semicontinuous process. Depending on the process conditions and type of process chosen, a heterogeneous catalyst can be slurried in the reaction mixture or can be used in a fixed bed. Research demands for alcoholysis include:

- optimisation of current technology;
- use of alternative, non-edible raw materials;
- new catalyst development;
- design of reliable small-scale production units;
- valorisation of glycerol;
- improvement of biodiesel oxidation stability; and
- development of cold-flow property improvers.

4.3. Process variables in transesterification

Transesterification transforms triglyceride molecules (90–98% of the oil), which are long and branched, into smaller esters whose size and physical properties are similar to those of diesel oils. The main factors affecting the transesterification reaction time and conversion and purity of the product esters are the molar ratio of alcohol to triglycerides, kind of alcohol, catalyst type and concentration, reaction conditions (temperature, pressure, mixing intensity, co-solvent) and degree of refinement of the vegetable oil (including FFA and water contents) There is also an effect of the nature of the glyceride [23,24].

Biodiesel and by-product yields are feedstock dependent. FAME yield, methanol consumption and glycerol/water production can be calculated for a given feedstock [25]. Basic quality parameters are acid value (AV), saponification value (SV), ester value (EV) and hydroxyl value (HV). EV denotes how many hydroxyl groups are esterified and HV how many such groups are free. Their sum therefore denotes the total number of hydroxyl groups. Any raw material used for biodiesel production can be evaluated on the basis of the AV, SV, EV and HV parameters. It has been shown that the FAME yield can be calculated as:

$$\text{FAME}\,(\text{kg}) = \frac{W}{3000K}(3000K + 45V + 38\text{AV} - 92\text{HV})$$

where W is sample weight (kg) and K is the relative molecular mass of KOH ($K = 56.11$). Fig. 3 effect of alcohol-to-oil ratio on product composition for transesterification.

4.4. Non-catalytic fatty acid alkyl ester production

In a catalytic reaction to produce biodiesel through transesterification, several processes, such as purification of the esters, separation and recovery of unreacted reactants and catalysts, are involved. These processes render production of biodiesel through a conventional catalytic transesterification system complicated, thus giving a reason to investigate the production of alkyl esters from vegetable oils via non-catalytic reactions. The absence of a catalyst simplifies a series of industrial process steps, and the production costs can be reduced. In addition, by-products such as fatty acid salts or free fatty acids are not formed, and thus fatty acid esters can be prepared at a high yield. Fig. 4 shows the schematic process of biodiesel fuel production by supercritical methanol [10].

4.5. Fatty acid esterification

Biodiesel can be produced by transesterification of triglycerides or by esterification of fatty acids. Esterification of carboxylic acids (specifically FFAs) is directly relevant to biodiesel synthesis given the increasing importance of low-cost lipid feedstocks containing high FFA concentrations. Esterification is a more facile reaction than transesterification because it allows easy elimination of a reaction product (water); this is not the case in high-temperature transesterification, where glycerol remains present and soluble. It follows that removal of water continuously from the reaction mixture is an important feature of the esterification process in order to shift the equilibrium towards the ester side. Fig. 5 shows different process schemes for the transformation of low and high FFA oils and fats into biodiesel.

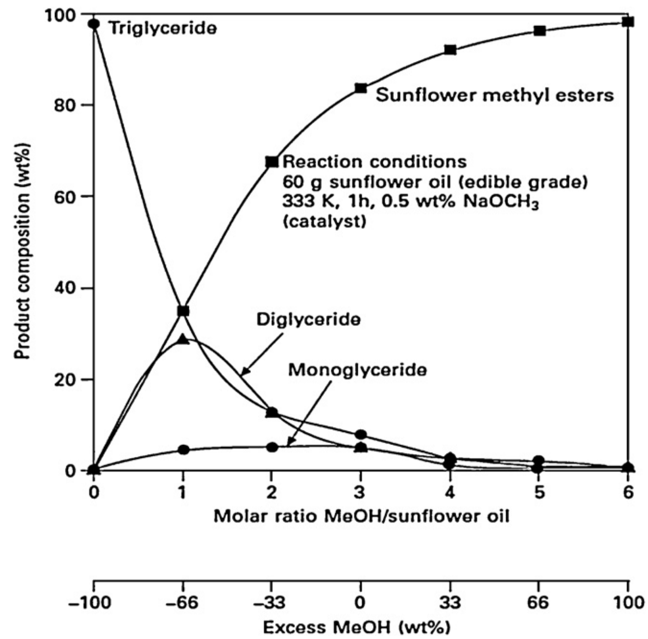


Fig. 3. Effect of alcohol-to-oil ratio on product composition for transesterification [26].

According to PCT Int. Publ. No. WO 2002/28811 A1 to Koncar and Mittelbach (to BDI) [27], an enhanced yield of fatty acid alkyl esters (FAAE) is obtained by separating the fatty acids, fatty acid salts and/or other fatty acid compounds contained in the glycerol

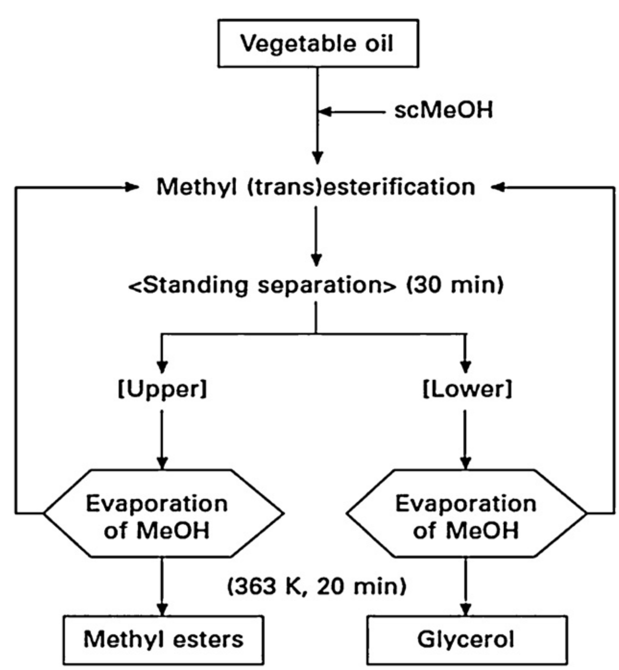


Fig. 4. Schematic process of biodiesel fuel production by supercritical methanol [24].

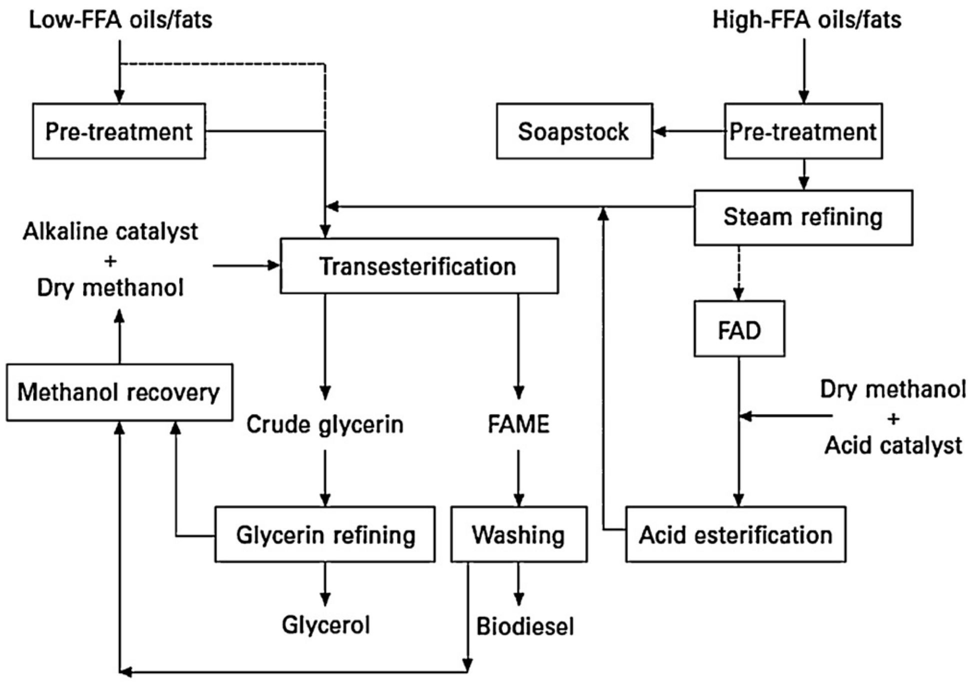


Fig. 5. Transformation of low- and high-FFA oils and fats into biodiesel by (trans) esterification.

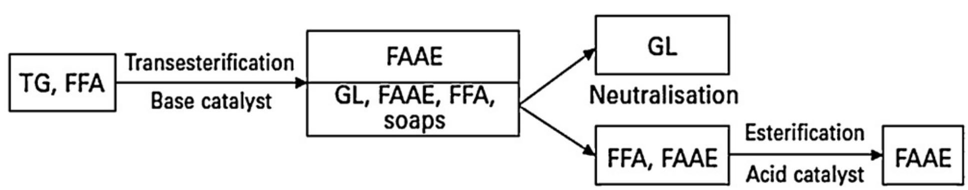


Fig. 6. Method for producing fatty acid alkyl esters from mixtures of triglycerides and fatty acids.

phase, resulting from base-catalysed transesterification of unrefined and recycled vegetable oils (typically CPO, RSO) or animal fats (>10 wt% FFA), by neutralisation, and subjecting the fatty acid phase to acid-catalysed post-esterification. The multistep processing mode is shown in Fig. 6.

4.6. Biodiesel catalysis

In order to achieve high ester yields in transesterification of vegetable oils in mild reaction conditions generally a catalyst is needed. Most commonly applied catalysts are alkaline or acidic materials. Typical liquid-phase catalysts used are NaOH, KOH, HCl, H_2SO_4 and HNO_3. Most heterogeneous catalysts may be grouped in five general categories: metallic (metals, transition metal compounds, organometallics and anchored metal complexes), solid bases and acids (including inorganic oxides such as Al_2O_3, SiO_2, $SiO_2{\cdot}Al_2O_3$, zeolites, ion-exchange resins, boria, phosphorus oxide, TiO_2, ZrO_2, Chromia, ZnO, MgO, CaO, SnO_x), natural catalysts such as coconut or palm ash. Table 3 shows different catalysts for conversion of sunflower oil (SNO) to methyl esters [28,29].

5. Alternative diesel fuels

Other processes can also be used to produce high-quality diesel fuel from vegetable oil or animal fat. Less appropriately, pyrolysis and hydrogenation products, diesel–vegetable oil blends, microemulsions of alcohols and water in vegetable oils and fermentation butanol are sometimes also referred to as biodiesel; in fact, they are just alternative (renewable) diesel fuels.

For use as diesel fuels vegetable oils and animal fats with high viscosity and low volatility must be modified in order to gain sufficient engine compatibility. Viscosity values of vegetable oils typically vary between 27.2 and 53.6 mm^2/s, whereas those of vegetable oil methyl esters are between 3.59 and 4.63 mm^2/s. Apart from transesterification with low alcohols (MeOH, EtOH) various other processes exist to improve the fuel combustion characteristics of biomass (in particular vegetable oils and fats) by reduction of viscosity:

- blending (dilution) of vegetable oil with other fuels (diesel, alcohols);
- microemulsification with short-chain alcohols (MeOH, EtOH);

Table 3
Experimental conversions of SNO to methyl esters for different catalysts.

Catalyst	Catalyst type	Conversion (%)
NaOH	Strongly basic	100.0
Amberlyst® A26 resin	Anion-exchange	0.1
Amberlyst® A27	Anion-exchange resin	0.4
Amberlyst® 15	Cation-exchange resin	0.7
MELCat XZO682/01	Sulphate doped zirconium hydroxide	0.0
MELCat XZO645/01	Silica doped zirconium hydroxide	0.0
TIS	Titanium silicate	0.6
TILCOM STC	Titanium chelate	0.5
$SnCl_2$	Lewis acid	3.0
MgO	Metallic oxide	11.0
USY-292	Zeolite	0.2
Novozym 435®[a]	Immobilised lipase	0.0

[a] *Candida antarctica*.

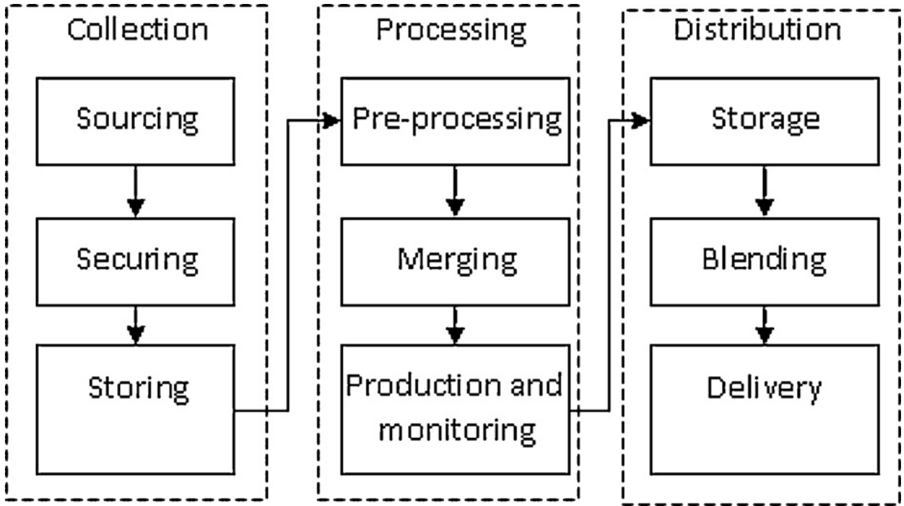


Fig. 7. Biodiesel production cycle model.

- thermal treatment (pyrolysis, gasification) producing alkanes, alkenes, carboxylic acids and aromatic compounds;
- catalytic cracking to (cyclo)alkanes;
- hydrotreating; and
- ozonation.

Among these primary technologies only dilution, microemulsification and heating do not chemically alter the raw material. Co-solvent blending of vegetable oils with other fuels like alcohol may bring the viscosity to within specification. Microemulsions cannot generally be recommended for long-term use in diesel engines. The development of stable bio-crude oil (BCO)/diesel oil emulsions is under way. Fig. 7 shows the biodiesel production cycle model [30,31].

5.1. Magnetically stabilised fluidised bed reactor

Guo et al. [32] proposed a novel production process of biodiesel using magnetically stabilised fluidised bed reactor (MSFBR) for cottonseed oil as shown in Fig. 8. The reactant flow rate and magnetic field intensity affects on the magnetic catalytic particles behaviour in the column were performed, and the transesterification reaction conditions of cottonseed oil were investigated in MSFBR with nanometer magnetic catalytic particles. Under the suitable reaction conditions of methanol/oil molar ratio 8:1, 40 $cm^3 min^{-1}$ flow rate, 225 Oe magnetic field intensity and temperature of 65 °C, the conversion efficiency reaches to 97% in 100 min. The stability and recovery of the magnetic catalytic particles in MSFBR are much better than that in autoclave stirred reactor.

5.2. Pyrolysis

Ito et al. [33] investigate the production of biodiesel from waste animal fats using pyrolysis method. It was found that the resulting triacylglycerols decompose at 360–390 °C, fatty acids were generated by cleavage of the ester bond, and short-chain hydrocarbons and short-chain fatty acids were generated by cleavage of the unsaturated bonds in the hydrocarbon chain. When the retention time was extended with a reaction temperature of 420 °C, light-oil hydrocarbons were generated by decarboxylation of the fatty acids. By adding palladium supported by activated carbon (Pd/C) as a catalyst, decarboxylation was promoted, and hydrocarbons comparable to light oil were selectively obtained in high yield at 85 wt.%. Compared to the biodiesel obtained by transesterification, the biodiesel obtained by pyrolysis showed improvement of about −5 °C in the pseudo-cold filter plugging point [33]. Viriya-empikul et al. [34] studied biodiesel production over Ca-based solid catalysts derived from industrial wastes.

5.3. Biodiesel production in heterogeneous transesterification

The biodiesel production in heterogeneous transesterification could be achieved by all CaO catalysts derived from eggshell, golden apple snail shell, and meretrix venus shell. The ascending order of the catalytic activity over the shell-derived catalysts (sequenced as eggshell, 94.1%FAME > golden apple snail shell, 93.2%FAME > meretrix venus shell, 92.3%FAME) was attributed to the decrease of specific surface areas and basic amount of the strong base sites. The optimum calcination temperature and time were 800 °C and 2–4 h, respectively. The shorter time and lower temperature caused the incomplete formation of active Ca-based

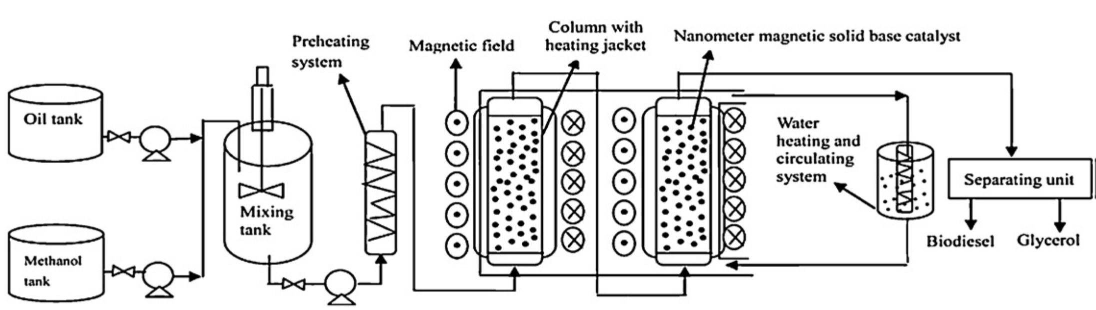


Fig. 8. Schematic diagram of continuous experiment system using MSFBR [32].



Fig. 9. Variable compression ratio (VCR) engine test setup.

catalysts, while the longer time and higher temperature caused the severe sintering of catalyst particles, resulting in suppressed biodiesel yields. These industrial wastes could stand for promising resources of low-cost catalysts which could bring about the lowcost biodiesel [34].

6. Case studies

Panwar et al. [35] studied the emissions performance of castor methyl ester (CME) on four strokes, single cylinder, variable compression ratio type diesel engine with three different blend i.e., B05, B10 and B20. Tests were carried out at a rated speed of 1500 rpm at different loads as shown in Fig. 9. It was concluded that the calorific value of pure CME is lower than that of diesel by about 15%. The blend B10 exhibits a calorific value about 45.50 MJ kg^{-1}, that is only 2% lower than that of diesel. With this blend engine develops better power when compared with power output with diesel. High power output is reported in many other studies it may be due to better lubricity which reduces friction loss and better combustion of blends. The trends of NO_X emission for CME are same as that of diesel at lower loads and slightly higher at full loads. Hence CME can be alternately used as fuel for diesel engine.

Panwar et al. [36] reported the CO_2 mitigation potential from castor seed oil in Indian. Context. If 10% of total production of castor seed oil is transesterified into biodiesel, then about 79,782 tones of CO_2 emission can be saved on annual basis. The CO_2 released during combustion of biodiesel can be recycled through next crop production, therefore, no additional burden on environment.

Ghobadian et al. [37] develop a model based on artificial neural network (ANN) for a diesel engine using waste cooking biodiesel fuel to predict the brake power, torque, specific fuel consumption and exhaust emissions of the engine. The data acquire from a two cylinders, four-stroke diesel engine was fuelled with waste vegetable cooking biodiesel and diesel fuel blends and operated at different engine speeds. It was found during the experiment that the blends of waste vegetable oil methyl ester with diesel fuel provide better engine performance and improved emission characteristics. Multi layer perception network (MLP) was used for non-linear mapping between the input and output parameters. It was observed that the ANN model can predict the engine performance and exhaust emissions quite well with correlation coefficient (R) 0.9487, 0.999, 0.929 and 0.999 for the engine torque, SFC, CO and HC emissions, respectively. The prediction MSE (Mean Square Error) error was between the desired outputs as measured values and the simulated values were obtained as 0.0004 by the model.

Peterson and Reece [38] studied the emission characteristics of ethyl and methyl ester of rapeseed oils with diesel control fuel. It was reported that the 100% rapeseed methyl ester (RME) and 100% rapeseed ethyl ester (REE) of hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO_X), were reduced to around 52.4, 47.6 and 10.0% respectively, but carbon dioxide (CO_2) and particulate matter (PM) were increased around 0.9, 9.9% respectively compared to the diesel control fuel. Also 100% REE reduced HC (8.7%), CO (4.3%) and NO_X (3.4%) compared to 100% RME.

Emission study of an automobile diesel engine fuelled with sunflower methyl ester was conducted by Munoz et al. [39]. It was found that the NO_X emission have been proved totally dependent on the engine operation with pure SFME (sunflower oil methyl ester). It was always larger than with diesel fuel and delaying the start of injection timing by 3° causes higher HC (hydrocarbons) with diesel fuel as well as with SFME.

The un-modified diesel engine was operated and it emission performance was conducted by Chhina et al. [40]. During the study it was found that, the combustible concentration of exhaust gases was found in the range of 0.1–0.167% for all the biodiesels and oxides of nitrogen (NO_X) were found 0.2–26% higher as compared to petro-diesel. It was also found that, the carbon monoxide emissions of all biodiesels to be 25–45% lower as compared to petro-diesel.

Puhan et al. [41] investigated Mahua oil ethyl ester was tested in 4-stroke direct injected natural aspirated diesel engine at constant speed of 1500 rev/min at different brake mean effective pressures. He observed that brake thermal efficiency of Mahua oil ethyl ester (MOEE) was comparable with diesel and it was observed that 26.36% for diesel whereas 26.42% for MOEE. Emission of carbon monoxide, hydrocarbons, oxides of nitrogen and Bosch smoke number where reduced around 58, 63, 12 and 70%, respectively in case of MOEE compared to diesel.

Hansen et al. [42] studied the exhaust NO_X emissions with biodiesel. It was found that, the reduction in torque varying from less than 0.5% to about 10% and exhaust NO_X emissions of biodiesel, 2% biodiesel were increase around 12 and 2.3% but ethanol–diesel fuel blend reduced NO_X emissions by 2.7% and was highly sensitive to load, with increased temperature and NO_X emissions at light load.

Szybist et al. [43] reported that the biodiesel can increase NO_X emission in engine with pump line nozzle fuel system due to its elevated bulk modules of compressibility. The NO_X effect can be circumvented (reduced) successfully by additisation with cetane improved, shifting the methyl oleate concentration in the biodiesel fuel or shifting the injection timing.

Lapuerta et al. [44] concluded that at partial load operation, no difference in power output, but increase in fuel consumption in the case of biodiesel would compensate its reduced heating value. At full load condition a certain decrease in power has been found with biodiesel. An increase in brake specific fuel consumption has been found when using biodiesel such as increase is generally in proportion to the reduction in heating value (9% in value base, 14% in mass basis) slight increase in NO_X emission when using biodiesel fuel. They have found sharp reduction in particulate emission with biodiesel as compared to diesel fuel. Other regulated emission such as those of total hydrocarbon (THC_s) and carbon monoxide (CO) are usually found to signification decreases with biodiesel.

Reddy et al. [45] prepared biodiesel from jatropha seed oil and tested with four stroke diesel engine at constant speed. It was conducted that, the *Jatropha curcas* L. seed oil can also be used as an alternative fuel for diesel engines up to B30 without any engine modifications. It was also found that B20 reveals better engine performance (high brake thermal efficiency and low sfc) in comparison with other blends.

The performance and emission of a diesel engine fuelled with Jatropha biodiesel oil and its blends was carried out by Chauhan et al. [46] as shown in Fig. 10. An experimental study reveals that

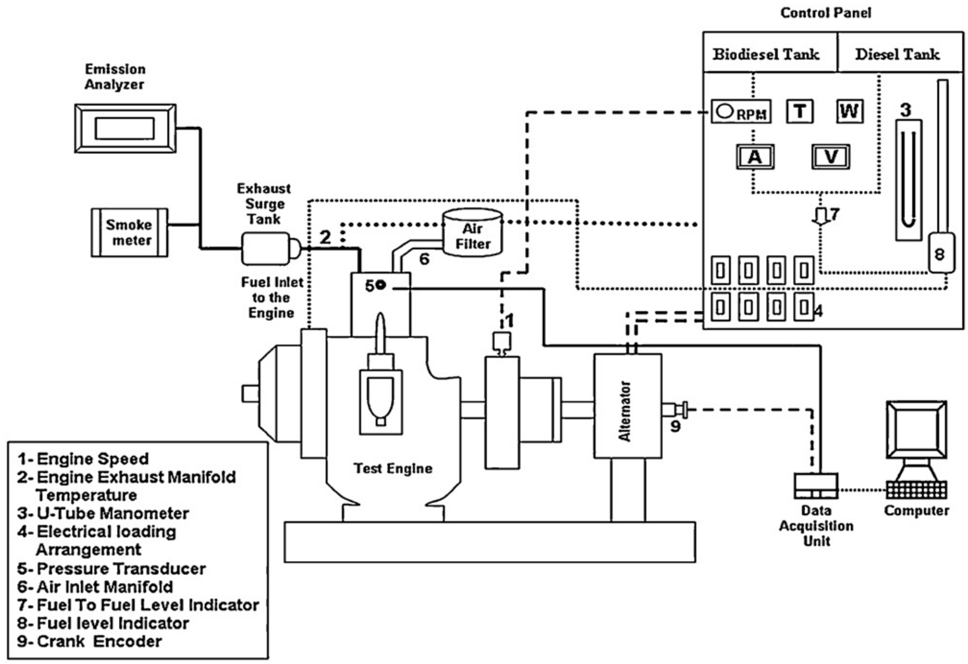


Fig. 10. Schematic of experimental setup [46].

brake thermal efficiency of Jatropha methyl ester and its blends with diesel were lower than diesel and brake specific energy consumption was found higher. HC, CO and CO_2 and smoke were found lower with Jatropha biodiesel fuel. NO_X emissions on Jatropha biodiesel and its blend were higher than diesel. The experiments suggest that biodiesel derived from non edible oil like Jatropha could be a good substitute to diesel fuel in diesel engine in the near future as far as decentralised energy production is concerned. In view of comparable engine performance and reduction in most of the engine emissions, it can be concluded and biodiesel derived from Jatropha and its blends could be used in a conventional diesel engine without any modification.

Performance and emission analysis of waste fried oil methyl esters (WFOME) was carried out on single-cylinder, four-stroke, direct injection, diesel engine by Hirkude and Padalkar [47]. The performance of the engine with diesel was considered as the baseline data. The performance parameters for different WFOME blends were found to be very close to diesel and the emission characteristics of engine improved significantly. At rated output, brake thermal efficiency of blend B50 (50% biodiesel + 50% mineral diesel) found 6.5% lower than that of diesel. For B50, brake specific consumption observed was 6.89% higher than that of diesel. CO emissions were reduced by 21–45% for different blends. The particulate matters were lower by 23–47%. Because of insignificant sulphur content, the sulphur dioxide emissions were lower by 50–100% for different blends [47].

Mallikappa et al. [48] studied performance of cardanol bio fuel blends with double cylinder CI engine. It was concluded from experimental studies that, the brake power increases (by 70% approximately) as load increases. Brake specific energy conversion decreases (by 25–30% approximately) with increase in brake power. Brake thermal efficiency increases with higher brake power and emission levels (HC, CO, NO_X) were nominal up to 20% blends.

Emission characteristics of a diesel engine fuelled with rice bran biodiesel and ethanol blends was investigated by Subbaiah and Gopal [49]. The experimental test results showed that the maximum brake thermal efficiency was obtained with 2.5% ethanol blended with RBD and are 6.98% and 3.93% higher than that of diesel fuel (DF) and biodiesel, respectively, at full load of the engine. Among the ethanol blends the minimum brake specific fuel consumption of 0.339 was observed with 2.5% ethanol. The exhaust gas temperature of the biodiesel was reduced by the ethanol blending. The lowest carbon monoxide, hydrocarbons and unused oxygen emissions were recorded with 2.5% ethanol blend. The smoke of the biodiesel was reduced by 20% when blended with 7.5% of ethanol. The intensity of sound with biodiesel and its ethanol blends was lower than that of DF at full load of the engine. The maximum reduction of smoke was 27.47% with 2.5% ethanol blending. Hence the 2.5% ethanol blended with biodiesel could improve the performance and reduce the emissions of the diesel engine.

Ozcanli et al. [50] investigate the performance of a three-cylinder, fourstroke, and direct-injection CI engine operated with terebinth (pistacia terebinthus) oil biodiesel. It was found that, exhaust emission profile of biodiesel fuels improved. CO and CO_2 emissions decreased up to 34.54% and 10.69% respectively. However, NO_X emissions increased up to 32.97%.

7. Conclusions

Biodiesel is being one of the promising fuels of the future for transportation vehicles. The renewability and environmental friendly combustion products are making the biodiesel more suitable for compression ignition engines.

Various edible, non-edible oils, animal fats can be used as feed stoke for the biodiesel production. The transesterification, pyrolysis and catalytic conversion processes was found suitable for the biodiesel production.

Number of known methods for the production of biodiesel are somehow limited by incomplete esterification of all fatty acids in the starting material, lengthy purification methods such as water washing, relatively long reaction times, contamination and separation difficulties associated with co-production of glycerol, and saponification of the starting material under certain reaction conditions.

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